

# Multilayer Adsorption of Interacting Polyatomics on Heterogeneous Surfaces

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## Abstract

In the present work we introduce a generalized lattice-gas model to study the multilayer adsorption of interacting polyatomics on heterogeneous surfaces. Using an approximation in the spirit of the well-known Brunauer–Emmet–Teller (BET) model, a new theoretical isotherm is obtained in one- and two-dimensional lattices and compared with Monte Carlo simulation. In addition, we use the BET approach to analyze these isotherms and to estimate the monolayer volume. In all cases, we found that the use of the BET equation leads to an underestimate of the true monolayer capacity. However, significant compensation effects were observed for heterogeneous surfaces and attractive lateral interactions.

*Key words:* Equilibrium thermodynamics and statistical mechanics, Surface thermodynamics, Adsorption isotherms, Monte Carlo simulations

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## 1 Introduction

The theoretical description of adsorption is a long-standing complex problem in surface science that presently does not have a general solution [1,2,3,4].

In 1918 Langmuir derived the monolayer adsorption isotherm kinetically for gas monoatomic molecules adsorbed on the homogeneous surface of adsorbents without attractions among the adsorbed molecules [5]. Later, some theories have been proposed to describe multilayer adsorption in equilibrium [6,7,8,9,10,11,12,13,14,15,16,17]. Among them, the one of Brunauer-Emmett-Teller (BET) [6] and the one of Frenkel-Halsey-Hill [7,8,9] are the simplest which provide the basis to construct more elaborate approaches. Those more elaborate analytic approaches take into account lateral interactions between the ad molecules, differences between the energy of the first and upper layers, surface energetic heterogeneity and so forth. These leading models have played an important role in the characterization of solid surfaces by means of gas adsorption.

A more accurate description of multilayer adsorption should account for the fact that, in practice, most adsorbates are polyatomic. Even the simplest non-spherical molecules such as  $N_2$  and  $O_2$  may adsorb on more than one site depending on the surface structure [17,18,19,20,21,22,23]. This effect, called multisite-occupancy adsorption, introduces a new complexity to the adsorption theory.

The difficulty in the analysis of the multisite statistics is mainly associated with three factors which differentiate the  $k$ -mers statistics from the usual single-particle statistics. Namely, *(i)* no statistical equivalence exists between particles and vacancies; *(ii)* the occupation of a given lattice site ensures that at least one of its nearest-neighbor sites is also occupied; and *(iii)* an isolated vacancy cannot serve to determine whether that site can ever become occupied.

However, several attempts were done in the past in order to solve the  $k$ -mers problem. Among them, Onsager [24], Zimm [25] and Isihara [26] made important contributions to the understanding of the statistics of rigid rods in dilute solution. The FH theory, due independently to Flory [27] and to Huggins [28], has overcome the restriction to dilute solution by means of a lattice calculation. The approach is a direct generalization of the theory of binary liquids in two dimensions or polymer molecules diluted in a monomeric solvent. It is worth mentioning that, in the framework of the lattice-gas approach, the adsorption of  $k$ -mers on homogeneous surfaces is an isomorphous problem to the binary solutions of polymer-monomeric solvent.

More recently, two new theories to describe adsorption with multisite occupancy have been introduced. In the first, Ramirez-Pastor et al. [29,30,31] pre-

sented a model to study the adsorption of linear adsorbates on homogeneous surfaces. The model is based on exact forms of the thermodynamic functions of linear adsorbates in one dimension and its generalization to higher dimensions. In the second, which is called the fractional statistical theory of the adsorption of polyatomics (FSTA), the configuration of the molecule in the adsorbed state is incorporated as a model parameter [32,33].

The treatments in Refs. [24,25,26,27,28,29,30,31,32,33] are limited in their application because they are valid only for monolayer adsorption. There are few studies that take into account multisite occupancy at the multilayer regime [34,35,36,37,38,39,40]. Aranovich and Donohue [34,35] presented a multilayer adsorption isotherm that should be capable to include multisite occupancy. Later, a closed exact solution for the multilayer adsorption isotherm of dimers was reported in Ref. [36]. It demonstrates that the determinations of surface areas and adsorption energies from polyatomic adsorbate adsorption (also called  $k$ -mers) may be misestimated, if this polyatomic character is not properly incorporated in the thermodynamic functions from which experiments are interpreted. This treatment has recently been extended [37] to include the two-dimensional nature of the substrate.

There are another two important physical facts which have not been sufficiently studied: 1) the effect of the lateral interactions between the ad-molecules and 2) the effect of surface heterogeneity in presence of multisite and multilayer adsorption. In the first case, a recent paper [38] extends the BET equation to include nearest-neighbor lateral interactions between the molecules adsorbed in the first layer. Following the configuration-counting procedure of the Bragg-Williams approach and the quasi-chemical approximation, Ref. [38] gives us a simple statistical mechanical framework for studying multilayer adsorption of interacting polyatomics. In the second case, multilayer adsorption of polyatomics on heterogeneous surfaces is a topic of interest in surface science since it comprises most features present in experimental situations. Surfaces generally present inhomogeneities due to irregular arrangement of surface and bulk atoms, the presence of various chemical species, etc. In this context, a recent job shows how the monolayer volume predicted by BET equation differs from its real value when considering both the adsorbate size and the surface topography [39].

On the other hand, combined effects coming from lateral interactions, multisite occupancy and surface heterogeneity have been analyzed in the interesting paper by Nikitas [40]. In Ref. [40], the author concludes that: (i) one can obtain an underestimation of the true monolayer capacity of the order of 25% when the adsorbate occupies more than one lattice site, and this underestimation will become worse if the effect of the multisite occupancy is coupled with heterogeneity effects and (ii) the attractive interactions in the gas adsorption lead always to a weak overestimation of the monolayer volume.

The previously discussed issues can be outlined in Fig. 1, where dimensions of complexity are sketched. In each axis we see a particular characteristic of the adsorption process that can (or cannot) be present in a particular model. Usually, the more features a model has, the more is its generality; and more complex the process it describes. In the multilayer regime, we can see models that include adsorption with lateral interactions, but they do not allow to multisite occupancy, or incorporate surface energetic heterogeneity, but they overlook lateral interactions in the adsorbed layer, etc. With Fig. 1 we try to show that, at present, some models venture in some of these dimensions of complexity but, the vast majority, lack the complete set of complexities. It is also clear that the farther away we are from the origin the more general (and usually the more complex) the model is. Even more, the upper plane (including multisite occupancy), is a set of models developed in the last decade that represent a leap forward in the lattice-gas theory.

In this work we will attempt to take one step further away from the origin, into a more general and encompassing scheme, presenting a model that considers the totality of these dimensions of complexity (multilayer adsorption, lateral interactions, multisite occupancy, energetic heterogeneity and surface topography). For this purpose, a theoretical formalism is presented based upon the analytical expression of the adsorption isotherm with lateral interaction weighted by the characteristic length of the surface heterogeneous. In addition, Monte Carlo (MC) simulations are performed in order to test the validity of the theoretical model. The new theoretical scheme allows us (1) to obtain an accurate approximation for multilayer adsorption on two-dimensional substrates accounting multisite occupancy, lateral interactions, energetic heterogeneity and surface topography, and (2) to provide a simple model from which experiments may be reinterpreted.

The present work is organized as follows. In Section II, we present the theoretical formalism. Section III is devoted to describing the simulation scheme. The analysis of the results and discussion are given in Section IV. Finally, the conclusions are drawn in Section V.

## 2 Model and theory

In this section, we will present the model and make a revision of some existing theories describing the adsorption process in the framework of the lattice-gas approximation. We will focus on those contributions that give contextualized understanding of the work that we will present.

## 2.1 Model

The substrate is modeled by a regular lattice of  $M$  sites with periodic boundary conditions, where the adsorption energy of the first layer  $\varepsilon_i^f$  depends on each site  $i$  of the surface and the adsorbate is represented by  $k$ -mers (linear particles that have  $k$  identical units). A  $k$ -mer adsorbed occupies  $k$  sites of the lattice and can arrange in many configurations. This property is called multisite-occupancy adsorption.

On the other hand, for higher layers, the adsorption of a  $k$ -mer is exactly onto an already absorbed one, with an adsorption energy of  $k\varepsilon$ . Thus, the monolayer structure reproduces in the remaining layers. The mechanism used to describe the adsorption in the multilayer regime mimics the phenomenon called pseudomorphism. This was observed, by using low-energy electron diffraction technique [41,42,43], in the case of adsorption of straight chain saturated hydrocarbon molecules on metallic surfaces. However, recent synchrotron X-ray scattering measurements show a different and more complex growth process in these systems [44]. Nevertheless, for simplicity, here we study a variant of the model that maintains the same mechanism to describe the adsorption in the higher layers. Because we analyze isotherms in the low coverage regime, we expect that this choice will not affect our results.

Finally, attractive and repulsive lateral interactions are considered in the first layer and horizontal interactions are ignored in higher layers. In this sense, although the contribution from the secondary adsorption can already be significant, the density of the molecules in the second and higher adlayers is expected to be much lower than that in the first adsorbed layer [BET equation can be applied at coverage not greatly exceeding (statistically) monolayer coverage]. Therefore, it seems to be satisfactorily enough to take into account only the interactions between the primarily adsorbed molecules [45].

Under these considerations we can write the Hamiltonian as:

$$H = \sum_{i=1}^M \varepsilon_i^f \sigma_i + k\varepsilon(N - N_1) + w \sum_{\langle i,j \rangle} \sigma_i \sigma_j - wN_1(k - 1), \quad (1)$$

where the first term of the right-hand side (RHS) represents the adsorption energy of the  $N_1$   $k$ -mers adsorbed in the first layer (adjacent to the adsorbent) and the second term is the energy of the  $(N - N_1)$   $k$ -mers adsorbed on top of the first layer (second layer, third layer, and so on). The third and fourth terms correspond to the lateral interaction energy, where  $w$  is the interaction energy between two nearest-neighbor (NN) units belonging to different  $k$ -mers adsorbed in the first layer (we use  $w > 0$  for repulsive and  $w < 0$  for attractive interactions);  $\sigma_i$  is the occupation variable which can take the values 0 if the

site  $i$  is empty or 1 if the site  $i$  is occupied and  $\langle i, j \rangle$  represents pairs of NN sites. Since the summation in the third term overestimates the total energy by including  $N_1(k-1)$  bonds belonging to the  $N_1$  adsorbed  $k$ -mers, the fourth term subtracts this exceeding energy.

Our study will be restricted to the class of lattice-gas models in which the substrate is a regular array of individual adsorption sites where molecules can be deposited (also in a discrete manner). In the following sections we will review some analytical deductions of those models. A more in depth treatment is carried out in the original publications.

## 2.2 Multilayer adsorption of non-interacting polyatomics on homogeneous surfaces

One way to begin our analysis is to review the behavior of a system of identical particles, which will be adsorbed in a regular lattice of  $M$  identical sites of adsorption [37]. The supposition is that, like in the BET model, adsorption is done on the surface of the solid or onto an already adsorbed particle. In this case, instead of adsorbing spherically symmetric ad-atoms, we will use entities (that we will call  $k$ -mers) that occupy  $k$  consecutive lattice sites.

Therefore, we will only have two possible unit-adsorption processes: (1) a  $k$ -mer occupies  $k$  consecutive empty surface sites; and (2) a  $k$ -mer adsorbs on top of an already adsorbed  $k$ -mer. This adsorptive process will form columns of  $k$ -mers on the solid. We must notice that a unit-adsorption where a  $k$ -mer adsorbs on top of two already adsorbed  $k$ -mers is prohibited.

In the case of the unit-desorption processes, we will only be able to desorb a  $k$ -mer that is on the top of one  $k$ -mer column or a  $k$ -mer that is adsorbed on the solid surface, but has no other  $k$ -mers adsorbed on top of it.

Under these conditions, the grand partition function of the system is:

$$\Xi = \sum_{n=0}^{n_{max}} \Omega_k(n, M) \xi^n, \quad (2)$$

where  $n_{max}(= M/k)$  is the maximum number of columns that can be formed,  $\Omega_k(n, M)$  it is the total number of distinguishable configurations of  $n$  columns in  $M$  sites and  $\xi$  is the grand partition function of a unique column of  $k$ -mers that has at least one  $k$ -mer in the first layer.

On the other hand, we have that the grand partition function for the monolayer

$(\Xi_1)$  is:

$$\Xi_1 = \sum_{n=0}^{n_{max}} \Omega_k(n, M) \lambda_1^n, \quad (3)$$

being  $n$ , in this case, the number of  $k$ -mers adsorbed on the surface of the solid (first layer), and  $\lambda_1$  the fugacity of the monolayer.  $\Omega_k(n, M)$  is still the number of possible configurations with  $n$   $k$ -mers in  $M$  sites. This quantity must be equal in Eqs. (2) and (3).

If now we compare Eqs. (2) and (3) we can observe that they have a similar form. This allows us to write:

$$\left( \frac{\partial \Xi}{\partial \xi} \right)_{M,T} = \left( \frac{\partial \Xi_1}{\partial \lambda_1} \right)_{M,T}. \quad (4)$$

If, in addition, inspired by this similarity, we propose the following ansatz:

$$\lambda_1 = \xi. \quad (5)$$

Then

$$\lambda_1 = \xi = \frac{cp/p_0}{1 - p/p_0} \Rightarrow \frac{p}{p_0} = \frac{1}{1 + c/\lambda_1}, \quad (6)$$

where  $c = q_1/q = \exp[-\beta k(\varepsilon^f - \varepsilon)]$  is the ratio between the partition function of a particle in the first layer and a particle in any other layer [ $\beta = (k_B T)^{-1}$ , being  $k_B$  the Boltzmann constant]. And, then, we can write the monolayer coverage as:

$$\theta_1 = \frac{k\bar{n}}{M} = \frac{k}{M} \lambda_1 \left( \frac{\partial \ln \Xi_1}{\partial \lambda_1} \right)_{M,T} \quad (7)$$

$$= \frac{k}{M} \xi \left( \frac{\partial \ln \Xi}{\partial \xi} \right)_{M,T}. \quad (8)$$

Now, the total coverage ( $\theta$ ) can be written in terms of the coverage of the monolayer ( $\theta_1$ ):

$$\theta = \frac{\theta_1}{1 - p/p_0}. \quad (9)$$

The theoretical procedure in Eqs. (6)-(9) provides the isotherm in the multilayer regime from the isotherm in the monolayer regime. In fact:

(1) By using  $\theta_1$  as a parameter ( $0 \leq \theta_1 \leq 1$ ), the relative pressure is obtained by using Eq. (6). This calculation requires the knowledge of an analytical expression for the monolayer adsorption isotherm.

(2) The values of  $\theta_1$  and  $p/p_0$  are introduced in Eq. (9) and the total coverage is obtained. The items (1) and (2) are summarized in the following scheme:

$$\begin{aligned} \theta_1 + \lambda_1(\theta_1) + \text{Eq. (6)} &\rightarrow p/p_0 \\ \Rightarrow \theta_1 + p/p_0 + \text{Eq. (9)} &\rightarrow \theta. \end{aligned}$$

Following the previous scheme, it is possible to obtain the exact multilayer isotherm for  $k$ -mers in 1D homogeneous surfaces. In fact, in Ref. [37] the expression for the monolayer coverage is proved to be:

$$p/p_0 = \frac{\theta_1 \left[1 - \frac{(k-1)}{k}\theta_1\right]^{k-1}}{kc(1 - \theta_1)^k + \left[1 - \frac{(k-1)}{k}\theta_1\right]^{k-1}}. \quad (10)$$

Equations (9) and (10) represent the exact solution of the 1D model and, as it is expected, retrieve the BET equation for the case  $k = 1$ .

Also, the previous scheme can be used to obtain an accurate approximation for multilayer adsorption on 2D substrates accounting multisite occupancy. In this case, the semi-empirical monolayer adsorption isotherm [33,46] can be used

$$\frac{p}{p_0} = \frac{\theta_1 \left[1 - \frac{(k-1)}{k}\theta_1\right]^{(k-1)\theta_1} \left[1 - \frac{2(k-1)}{\zeta k}\theta_1\right]^{(k-1)(1-\theta_1)}}{zkc(1 - \theta_1)^k + \theta_1 \left[1 - \frac{(k-1)}{k}\theta_1\right]^{(k-1)\theta_1} \left[1 - \frac{2(k-1)}{\zeta k}\theta_1\right]^{(k-1)(1-\theta_1)}}, \quad (11)$$

where  $\zeta$  is the connectivity of the lattice and  $z$  represents the number of available configurations (per lattice site) for a linear  $k$ -mer at zero coverage. Thus,  $z = 1$  for  $k = 1$  and  $z = \zeta/2$  for  $k \geq 2$ .

Note that, for  $\zeta = 2$ , Eq. (11) is identical to the Eq. (10). Therefore, Eqs. (9) and (11) represent the general solution of the problem of multilayer adsorption in homogeneous surfaces with multisite occupancy.

In the following section our aim will be to generalize this expression to include the lateral interactions following the methodology used in Ref. [38]. Clearly, the complexity of the isotherm is greatly increased, but the expression is still



a manageable one and in the case of zero interactions the previous case is retrieved.

### 2.3 Multilayer adsorption of interacting polyatomics on homogeneous surfaces

Due to the complexity introduced in the analytical expressions because of the lateral interactions is that approximations are used to deal with this feature of the adsorption process. The most commonly used approximations are the *mean-field approximation* (MFA) [45,47] and the *quasi-chemical approximation* (QCA) [45,47].

As shown in previous work[47], the configuration-counting procedure<sup>2</sup> of the QCA allows us to obtain an approximation that is significantly better than the MFA for polyatomics. Based on this finding, we restrict the rest of our discussion to the estimates obtained under QCA.

In order to apply the theoretical scheme described in previous section, we start with the monolayer adsorption isotherm of interacting  $k$ -mers adsorbed on a lattice of connectivity  $\zeta$  obtained from the formalism of QCA [47],

$$\lambda_1 = \left[ \frac{\theta_1 \exp(\beta w z / 2)}{k \eta(\zeta, k) \left(\frac{z}{\zeta}\right)^{2(k-1)}} \right] \left[ \frac{(1 - \theta_1)^{k(\zeta-1)} [k - (k-1)\theta_1]^{k-1} \left[\frac{z\theta_1}{2k} - \alpha\right]^{z/2}}{\left[\frac{\zeta k}{2} - (k-1)\theta_1\right]^{k-1} \left[\frac{\zeta}{2}(1 - \theta_1) - \alpha\right]^{k\zeta/2} \left(\frac{z\theta_1}{\zeta k}\right)^z} \right], \quad (12)$$

where

$$z = [2(\zeta - 1) + (k - 2)(\zeta - 2)], \quad (13)$$

$$\alpha = \frac{z\zeta}{2k} \frac{\theta_1(1 - \theta_1)}{\left[\frac{\zeta}{2} - \left(\frac{k-1}{k}\right)\theta_1 + b\right]}, \quad (14)$$

$$b = \left\{ \left[ \frac{\zeta}{2} - \left(\frac{k-1}{k}\right)\theta_1 \right]^2 - \frac{z\zeta}{k} A \theta_1(1 - \theta_1) \right\}^{1/2}, \quad (15)$$

and

$$A = 1 - \exp(-\beta w). \quad (16)$$

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<sup>2</sup> The important assumption in this method is that pairs of NN sites are treated as if they were independent of each other (this assumption is, of course, not true, because the pairs overlap [45]).

Replacing Eq. (12) into Eq. (6), we obtain

$$\left(\frac{p}{p_o}\right)^{-1} = 1 + \frac{ck\eta(\zeta, k) \left(\frac{2}{\zeta}\right)^{2(k-1)} \left[\frac{\zeta k}{2} - (k-1)\theta_1\right]^{k-1} \left[\frac{\zeta}{2}(1-\theta_1) - \alpha\right]^{k\zeta/2} \left(\frac{z\theta_1}{\zeta k}\right)^z}{\theta_1 \exp(\beta wz/2)(1-\theta_1)^{k(\zeta-1)} [k - (k-1)\theta_1]^{k-1} \left[\frac{z\theta_1}{2k} - \alpha\right]^{z/2}}. \quad (17)$$

Eqs. (9) and (17) represent the solution describing the multilayer adsorption of interacting  $k$ -mers on homogeneous surfaces in the framework of the QCA. This method is presented in more depth in [38].

Now we can see that we have moved upward in the plane of complexity and further more included interactions. The next section revises the role of surface heterogeneity and lateral interactions.

#### 2.4 Multilayer adsorption of interacting polyatomics on heterogeneous surfaces

In the two previous sections, we obtained the multilayer isotherm from the monolayer isotherm. It is possible demonstrate that this formalism still holds for interacting  $k$ -mers and a given surface heterogeneity. However, this strategy leads to a complex solution that is not useful for practical purposes. To build a simpler function (easier to analyze), we have chosen to approximate the multilayer heterogeneous isotherm by a weighted sum of multilayer homogeneous isotherms.

The heterogeneous surface is modeled by two kinds of adsorption sites in the first layer (bivariate surface): strong sites with adsorption energy  $\varepsilon_1^f$  and weak sites with adsorption energy  $\varepsilon_2^f$ . As seen later, these sites can be spatially distributed in different ways (different topographies). Then, the total adsorption energy for an isolated  $k$ -mer on the first layer with  $k_1$  monomers located over strong sites and  $k_2$  monomers located over weak sites is

$$E_i = k_1\varepsilon_1^f + k_2\varepsilon_2^f. \quad (18)$$

Under these considerations, and using the formalism of the integral equation of the adsorption isotherm [17], the mean coverage  $\theta$  can be written as

$$\theta = \sum_{E_i} f(E_i)\theta_{\text{loc}}(E_i), \quad (19)$$

where  $f(E_i)$  is the fraction of  $k$ -uples of  $k_1$  strong sites and  $k_2$  weak sites ( $k_1 + k_2 = k$ ) and  $\theta_{\text{loc}}(E_i)$  represents the local multilayer adsorption isotherm

corresponding to an adsorptive energy  $E_i$ . This local isotherm can be well approximated by using the multilayer adsorption isotherm associated to an homogeneous surface characterized by an effective value of  $c$  given by

$$c_i = \exp [-\beta (E_i - k\varepsilon)]. \quad (20)$$

This value of  $c_i$  can also be expressed as function of  $c_1$  and  $c_2$ , the values of  $c$  for homogeneous surfaces whose adsorption energies are  $\varepsilon_1^f$  and  $\varepsilon_2^f$ , respectively. Thus, if the  $i$ -th term in Eq. (19) corresponds to a  $k$ -mer with  $k_1$  units located over strong sites and  $k_2$  units located over weak sites, then

$$c_i = (c_1^{k_1} c_2^{k_2})^{1/k}. \quad (21)$$

As an example, let us consider the multilayer adsorption of non-interacting dimers on a bivariate linear lattice, where strong and weak sites are spatially distributed in alternating homotattic patches of size  $l$  ( $l = 1, 2, 3, \dots$ ). In this case, Eq. (19) has three different terms, being each one of them a dimer isotherm<sup>3</sup> with a particular value of  $c$ ,

$$\begin{aligned} \theta = & \left( \frac{l-1}{2l} \right) \frac{1}{(1-p/p_0)} \left\{ 1 - \left[ \frac{1-p/p_0}{1+(4c_1-1)p/p_0} \right]^{1/2} \right\} + \\ & + \left( \frac{1}{l} \right) \frac{1}{(1-p/p_0)} \left\{ 1 - \left[ \frac{1-p/p_0}{1+(4\sqrt{c_1 c_2}-1)p/p_0} \right]^{1/2} \right\} + \\ & + \left( \frac{l-1}{2l} \right) \frac{1}{(1-p/p_0)} \left\{ 1 - \left[ \frac{1-p/p_0}{1+(4c_2-1)p/p_0} \right]^{1/2} \right\}. \end{aligned} \quad (22)$$

The first [third] term in the RHS of Eq. (22) represents the adsorption within a strong [weak] patch, on a pair of sites  $(\varepsilon_1^f, \varepsilon_1^f)$  [ $(\varepsilon_2^f, \varepsilon_2^f)$ ], with  $c_1$  [ $c_2$ ]. The fraction of  $(\varepsilon_1^f, \varepsilon_1^f)$  [ $(\varepsilon_2^f, \varepsilon_2^f)$ ] pairs on the lattice is  $(l-1)/2l$  [48]. The remaining term of Eq. (22) corresponds to a dimer isotherm on a  $(\varepsilon_1^f, \varepsilon_2^f)$  [or  $(\varepsilon_2^f, \varepsilon_1^f)$ ] pair ( $c = \sqrt{c_1 c_2}$ ), being  $1/l$  the fraction of this kind of pairs on the lattice. As it can be observed, Eq. (22) depends on  $l$  and the dimer isotherm *sees* the topography.

In general, the number of terms in Eq. (19) increases as the adsorbate size  $k$  is increased and this equation leads to a complex solution. This scheme can be notoriously simplified following the results in Ref. [39]. In this paper, the authors showed that:

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<sup>3</sup> In the particular case of  $k = 1$  and  $k = 2$ , it is possible to solve Eqs. (9) and (10) to obtain single expressions of the multilayer isotherms corresponding to monomers and dimers.

- If  $k \gg l$  (with  $k > 1$ ), the multilayer adsorption isotherm can be represented by a single homogeneous isotherm

$$\theta = \theta_{\text{loc}}(\sqrt{c_1 c_2}). \quad (23)$$

- For a topography where  $k \ll l$ , the isotherm is

$$\theta = \frac{1}{2}\theta_{\text{loc}}(c_1) + \frac{1}{2}\theta_{\text{loc}}(c_2). \quad (24)$$

- The details of the topography are relevant only when  $k \sim l$ . In this case, it is possible to consider a simpler expression of the multilayer isotherm given by

$$\theta = \left(\frac{l-1}{2l}\right)\theta_{\text{loc}}(c_1) + \left(\frac{1}{l}\right)\theta_{\text{loc}}(\sqrt{c_1 c_2}) + \left(\frac{l-1}{2l}\right)\theta_{\text{loc}}(c_2). \quad (25)$$

Eq. (25) (i) captures the extreme behaviors Eqs. (23) and (24), and (ii) approximates very well the complete Eq. (19) in 1D and 2D. In the 2D case, the local isotherm in Eq. (25) is obtained from Eqs. (9) and (11), with  $\zeta = 3, 4$  and  $6$  for honeycomb, square and triangular lattices, respectively.

Finally, we propose to extend Eq. (25) as to describe multilayer adsorption of interacting polyatomic molecules on heterogeneous surfaces. For this purpose, we propose to obtain the local isotherms from Eqs. (9) and (17). The advantages of using this simple description as a tool for interpreting multilayer adsorption data and characterization of the adsorption potential will be shown in Section 4 by analyzing simulation results.

### 3 Monte Carlo simulation

The adsorption process is simulated through a grand canonical ensemble Monte Carlo (GCEMC) method.

For a given value of the temperature  $T$  and chemical potential  $\mu$ , an initial configuration with  $N$   $k$ -mers adsorbed at random positions (on  $kN$  sites) is generated. Then, an adsorption-desorption process is started, where each elementary step is attempted with a probability given by the Metropolis [49] rule:

$$W = \min \{1, \exp [-\beta (\Delta H - \mu \Delta N)]\}, \quad (26)$$

where  $\Delta H$  and  $\Delta N$  represent the difference between the Hamiltonians and the variation in the number of particles, respectively, when the system changes

from an initial state to a final state. In the process there are four elementary ways to perform a change of the system state, namely, adsorbing one molecule onto the surface, desorbing one molecule from the surface, adsorbing one molecule in the bulk liquid phase and desorbing one molecule from the bulk liquid phase. In all cases,  $\Delta N = \pm 1$ .

The algorithm to carry out one MC step (MCS), is the following :

- 1) Set the value of the chemical potential  $\mu$  and the temperature  $T$ .
- 2) Set an initial state by adsorbing  $N$  molecules in the system. Each  $k$ -mer can adsorb in two different ways: *i*) on a linear array of  $(k)$  empty sites on the surface or *ii*) exactly onto an already adsorbed  $k$ -mer.
- 3) Introduce an array, denoted as  $A$ , storing the coordinates of  $n_e$  entities, being  $n_e$ ,

$$n_e = \text{number of available adsorbed } k\text{-mers for desorption (n}_d\text{)} \\ + \text{number of available } k\text{-uples for adsorption (n}_a\text{)}, \quad (27)$$

where  $n_a$  is the sum of two terms: *i*) the number of  $k$ -uples of empty sites on the surface and *ii*) the number of columns of adsorbed  $k$ -mers<sup>4</sup>.

- 4) Choose randomly one of the  $n_e$  entities, and generate a random number  $\xi \in [0, 1]$ 
  - 4.1) if the selected entity is a  $k$ -uple of empty sites on the surface then adsorb a  $k$ -mer if  $\xi \leq W_{ads}^{surf}$ , being  $W_{ads}^{surf}$  the transition probability of adsorbing one molecule onto the surface.
  - 4.2) if the selected entity is a  $k$ -uple of empty sites on the top of a column of height  $i$ , then adsorb a new  $k$ -mer in the  $i + 1$  layer if  $\xi \leq W_{ads}^{bulk}$ , being  $W_{ads}^{bulk}$  the transition probability of adsorbing one molecule in the bulk liquid phase.
  - 4.3) if the selected entity is a  $k$ -mer on the surface then desorb the  $k$ -mer if  $\xi \leq W_{des}^{surf}$ , being  $W_{des}^{surf}$  the transition probability of desorbing one molecule from the surface.
  - 4.4) if the selected entity is a  $k$ -mer on the top of a column then desorb the  $k$ -mer if  $\xi \leq W_{des}^{bulk}$ , being  $W_{des}^{bulk}$  the transition probability of desorbing one molecule from the bulk liquid phase.
- 5) If an adsorption (desorption) is accepted in 4), then, the array  $A$  is updated.
- 6) Repeat from step 4)  $M$  times.

In the present case, the equilibrium state could be well reproduced after discarding the first  $m \approx 10^6 MCS$ . Then, averages were taken over  $m' \approx 10^6 MCS$  successive configurations. The total coverage was obtained as simple averages,

$$\theta = \frac{k \langle N \rangle}{M}, \quad (28)$$

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<sup>4</sup> Note that the top of each column is an available  $k$ -uple for the adsorption of one  $k$ -mer.

where  $\langle N \rangle$  is the mean number of adsorbed particles, and  $\langle \dots \rangle$  means the time average over the MC simulation runs.

## 4 Results and discussion

In the present section, we will analyze the main characteristics of the multilayer adsorption isotherms given by Eq. (25) [with local isotherms obtained from Eqs. (9) and (17)], in comparison with simulation results for a lattice-gas of interacting  $k$ -mers on heterogeneous one-dimensional and square lattices.

Heterogeneity is introduced by considering bivariate surfaces, i.e., surfaces composed by two kinds of sites in the first layer, strong and weak sites, with adsorptive energies  $\varepsilon_1^f$  and  $\varepsilon_2^f$ , respectively. Recent developments in the theory of adsorption on heterogeneous surfaces, like the supersite approach [50], and experimental advances in the tailoring of nanostructured adsorbates [51,52], encourage this kind of study. A special class of bivariate surfaces, with a chessboard structure, has been observed recently to occur in a natural system [53], although it was already intensively used in modeling adsorption and surface diffusion phenomena [48,54,55,56].

Bivariate surfaces may also mimic, to a rough approximation, more general heterogeneous adsorbates. Just to give a few examples, we may mention the surfaces with energetic topography arising from a continuous distribution of adsorptive energy with spatial correlations, like those described by the dual site-bond model [57], or that arising from a solid where a small amount of randomly distributed impurity (strongly adsorptive) atoms are added [58]. In both cases the energetic topography could be roughly represented by a random spatial distribution of irregular patches (with a characteristic size) of weak and strong sites.

In the particular case studied in this article, the surface is modeled in two different ways: (1) as a chain of alternating patches of size  $l$  (see Fig. 2a); and (2) as a collection of finite homotattic patches in a chessboard-like array, where each patch is assumed to be a domain of equal size,  $l \times l$  sites (see Fig. 2b). In this model, the energy correlation length is simply given by the patch size.

The computational simulations have been developed for one-dimensional chains of  $10^4$  sites, and square  $L \times L$  lattices with  $L = 144$ , and periodic boundary conditions. With this lattice size we verified that finite-size effects are negligible. Note, however, that the linear dimension  $L$  has to be properly chosen in such a way that it is a multiple of  $l$ .

We start analyzing what happens when the topography is changed. Fig. 3 shows the behavior of the multilayer adsorption isotherms for  $k = 2$ ,  $\beta w = -1$  and different topographies in 1D as indicated. The energy difference between different patches has been chosen to be high ( $c_1 = 1000$  and  $c_2 = 1$ ) in order to emphasize the effects of the surface heterogeneity. We have identified the different topographies as  $l_C$  for patches of size  $l$ , and  $bp$  for the case of a surface with two big patches ( $l \rightarrow \infty$ ). Symbols represent simulation results and lines correspond to theoretical data [Eq. (25)]. It can be seen that all curves are contained between the two limit ones: the one corresponding to  $1_C$  and the one corresponding to  $bp$ .

For  $l = 1$ , the adsorption energy of a dimer in the first layer is  $\varepsilon_1^f + \varepsilon_2^f$  for all configuration. In this condition, the system corresponds to a 1D lattice-gas of interacting dimers on a homogeneous surface and, consequently, Eq. (25) is exact.

In general, for  $l > 1$ , this equation is approximate. For  $l = 2$ , the analytic isotherms agree very well with the simulation data. However, for  $p/p_0$  ranging between 0 and 0.15, some differences between theoretical and numerical data are observed. This happens because Eq. (25) has been built assuming that the three different pairs of sites are filled simultaneously and independently. However, for  $c_1 \gg c_2$ , the real process occurs in 3 stages: (i) the pairs of sites  $(\varepsilon_1^f, \varepsilon_1^f)$  are covered; (ii) the pairs  $(\varepsilon_2^f, \varepsilon_2^f)$  begin to be filled and (iii) the multilayer is formed. Note that in the first stage all the pair of sites  $(\varepsilon_1^f, \varepsilon_2^f)$  and  $(\varepsilon_2^f, \varepsilon_1^f)$  are removed. For this regime, a better approximation can be obtained by a semisum of two isotherms with  $c_1$  y  $c_2$ .

When  $l = 3$ , the agreement between the analytic isotherms and the simulation data is very good. In this case, for  $c_1 \gg c_2$  the first stage does not eliminate all the pairs of sites  $(\varepsilon_1^f, \varepsilon_2^f)$  and  $(\varepsilon_2^f, \varepsilon_1^f)$ , because each dimer occupies only two sites in the strong patches. For this reason, the range of validity of Eq. (25) is wider than in the previous case. Now, if  $l = 4$  or  $l = 5$ , the behaviors are similar to those observed for  $l = 2$  or  $l = 3$ , respectively. In general, for even  $l$ , the first stage eliminates almost completely the pairs of sites  $(\varepsilon_1^f, \varepsilon_2^f)$  and  $(\varepsilon_2^f, \varepsilon_1^f)$ , while this does not happen for odd  $l$ . Finally, when  $l \rightarrow \infty$ , the fraction of pair  $(\varepsilon_1^f, \varepsilon_2^f)$  and  $(\varepsilon_2^f, \varepsilon_1^f)$  goes to zero and Eq. (25) is exact. This limit corresponds to the called large patches topography ( $bp$  surface in our model), where the surface is assumed to be a collection of homogeneous patches, large enough to neglect border effects between neighbor patches with different adsorption energies.

We now analyze the effect of the lateral interactions on the behavior of the system. For this purpose, Fig. 4 shows the adsorption isotherms for  $k = 2$ ,  $c_1 = 1000$ ,  $c_2 = 1$  and two different values of the lateral interactions  $\beta w = -1$  (attractive case) and  $\beta w = 1$  (repulsive case). In addition, for each value of

$\beta w$ , the limit topographies ( $1_C$  and  $bp$ ) have been considered (as seen in Fig. 3, all curves corresponding to all topographies are contained between them).

For repulsive couplings, the interactions do not favor the adsorption on the first layer and the isotherms shift to higher values of pressure. On the other hand, attractive lateral interactions facilitate the formation of the monolayer. Consequently, the isotherms shift to lower values of  $p/p_o$  and their slope increases as the ratio  $|\beta w|$  increases. In both cases ( $\beta w = -1$  and  $\beta w = 1$ ), the agreement between theoretical and simulation data is excellent.

From the curves in Fig. 4 (and from data not shown here for the sake of clarity) it is observed that: there exists a wide range of  $\beta w$ 's ( $-2 \leq \beta w \leq 2$ ), where the theory provides an excellent fitting of the simulation data. In addition, most of the experiments in surface science are carried out in this range of interaction energy. Then, the present theory not only represents a qualitative advance in the description of the multilayer adsorption of interacting  $k$ -mers on heterogeneous surfaces, but also gives a framework and compact equations to consistently interpret thermodynamic multilayer adsorption experiments of polyatomic species such as alkanes, alkenes, and other hydrocarbons on regular surfaces.

The effect of energetic heterogeneity (ratio between  $c_1$  and  $c_2$ ) is analyzed in Fig. 5, where the degree of heterogeneity is varied by changing the value of  $c_2$  between 1 and 100 with  $c_1$  fixed ( $c_1 = 1000$ ). As in Fig. 4,  $k = 2$  and  $\beta w = -1$ . Lines represent theoretical results and symbols correspond to simulation data ( $c_2 = 1$ : circles;  $c_2 = 10$ : triangles; and  $c_2 = 100$ : squares). For each set of values of the parameters, the limit cases corresponding to  $1_C$  (open symbols) and  $bp$  (solid symbols) topographies are studied. As it can be observed from the simple inspection of the figure, the effect of topography is important in a range of  $c_2/c_1$  between  $10^{-3}$  and  $10^{-2}$  and is practically negligible for  $10^{-1} < c_2/c_1 < 1$ .

To complete the discussion started in Fig. 3, we now evaluate the effect of the  $k$ -mer size on the adsorption isotherms. This study is shown in Fig. 6, where the  $1_C$  and  $bp$  multilayer adsorption isotherms are plotted for  $\beta w = -1$ ,  $c_1 = 1000$ ,  $c_2 = 1$  and two different values of  $k$  ( $k = 2$  and  $k = 10$ ). One important conclusion can be drawn from the figure. Namely, the effects of topography and energetic heterogeneity tends to disappear as the size  $k$  is increased.

The study in Figs. 3-6 was repeated for surfaces in 2D. The behavior of the curves (not shown here for brevity) is very similar to the one observed in 1D.

Summarizing, we have shown that just by using an expression of three terms, Eq. (25), we can approach very well the multilayer isotherm in 1D and 2D for the adsorption of interacting polyatomics on heterogeneous surfaces. In the



next, we will use this approximation and Monte Carlo simulations to study how lateral interactions, multisite occupancy and surface heterogeneity affect the determination of monolayer volume predicted by the BET equation.

In a typical experiment of adsorption, the adsorbed volume of the gas,  $v$ , is measured at different pressures and at a given fixed temperature, the total coverage is  $\theta = v/v_m$ . Analyzing an isotherm with the BET equation

$$\theta = \left( \frac{1}{1 - p/p_0} \right) \left( \frac{cp/p_0}{1 - p/p_0 + cp/p_0} \right), \quad (29)$$

it is possible to estimate the monolayer volume if we rewrite the previous equation as:

$$\frac{p/p_0}{v(1 - p/p_0)} = \frac{1}{cv_m} + \frac{(c - 1)}{cv_m} p/p_0. \quad (30)$$

This equation is a linear function of  $p/p_0$ . If we denote with  $a$  and  $b$ , the  $y$ -intercept and the slope of this straight line, respectively, we obtain

$$v_m^* = \frac{1}{a + b} \quad (31)$$

and

$$c^* = \frac{b}{a} + 1. \quad (32)$$

The asterisk has been added in order to indicate that the quantities given by Eqs. (31) and (32) correspond to the prediction of the BET theory. Then, by means of a plot (the so-called BET plot) of the experimental data of  $\frac{p/p_0}{v(1 - p/p_0)}$  vs  $p/p_0$ , we can obtain an estimate of the monolayer volume and the parameter  $c$ . Nevertheless, in the experiments it is commonly found that there are deviations from linearity in the BET plot.

Following the scheme described in previous paragraphs, we carry out numerical experiments to determine, in different adsorption situations, how much the value of the monolayer volume predicted by the BET equation differs from its real value,  $v_m$ . With this purpose, analytic and simulation isotherms were analyzed as experimental data. In this way, we have determined how adsorbate size, surface heterogeneity and lateral interactions, affect the standard determination of the monolayer volume.

In Fig. 7 we plot the calculated value of  $v_m^*/v_m$  as a function of  $k$  for fixed values of  $c_1$  and  $c_2$  (namely  $c_1 = 1000$  and  $c_2 = 1$ ) and different values of

the attractive lateral interaction. The repulsive interactions, not shown in the figure, show a marked deviation from the predicted BET equation, therefore wiping out compensation effects due to the surface heterogeneity.

We can see three sets of plots in Fig. 7. Each set (1) is the result of the effect of different lateral interactions strengths:  $\beta w = 0$ , circles;  $\beta w = -0.5$ , squares and  $\beta w = -1.0$ , triangles; and (2) depicts the limiting cases for the surface topography: open and solid symbols correspond to  $1_C$  and  $bp$  surfaces, respectively. All other topographies must lay in between those two plots.

If we analyze the behavior of the open symbols, we are analyzing, essentially, the homogenous case [39] where an already known feature for the homogeneous scenario can be distinguished: the compensation effect of  $k$  is lower as  $k$  increases, as [37] stated for the non-interacting case. On the other hand, for  $bp$  surfaces, the compensation effect increases with  $k$  as seen in [39]. In all cases, for stronger (attractive) interaction strength the plots move upwards showing greater compensation effects.

As shown in previous work [36,37] for non-interacting  $k$ -mers on homogeneous surfaces, the monolayer volume from the BET model diminishes with increasing values of the  $k$ -mer size. The data presented in Fig. 7 demonstrate that attractive lateral interactions and surface heterogeneity play a key role in the compensation of  $k$ -mer size effects. This finding is very important because most of the experiments in surface science are carried out in these conditions.

Finally, the study in Fig. 7 is repeated for 2D surfaces (see Fig. 8). In this case, both the compensation effect for attractive interactions and the underestimation of the monolayer volume for repulsive interactions (not shown here) are more important than in the 1D case. The explanation is simple: in 1D systems, particles will interact only at their ends, regardless of  $k$ ; on the other hand, in 2D systems, each particle interacts at their ends, but also interacts along its  $k$  monomers. This makes the interaction energy grow linearly with  $k$  (if all first neighbors are occupied), and indicates that lateral interactions will play a more important role in two-dimensional adsorption systems than in one-dimensional ones.

## 5 Conclusions

In this work, we have studied the multilayer adsorption of interacting polyatomic molecules onto heterogeneous surface. The polyatomic character of the adsorbate was modeled by a lattice gas of  $k$ -mers. With respect to lateral interactions, the ad-ad couplings in the monolayer were explicitly considered in the solutions. The range of validity of analytical isotherms was analyzed by

comparing theoretical and MC simulation results.

We also analyzed the 1D and 2D BET plots obtained using the theoretical and simulation isotherms. For non-interacting  $k$ -mers, we found that the use of BET equation leads to an underestimate of the true monolayer volume: this volume diminishes as  $k$  is increased. The situation is different for the case of interacting molecules over heterogeneous surface. Thus, attractive lateral interactions favor the formation of the monolayer and, consequently, compensate the effect of the multisite occupancy. In this case, the monolayer volume predicted by BET equation agrees very well with the corresponding true value. In the case of repulsive couplings, the lateral interactions impede the formation of the monolayer and the BET predictions are bad (even worse than those obtained in the non-interacting case). Both the compensation effect for attractive interactions and the underestimation of the monolayer volume for repulsive interactions are more important for 2D systems.

## 6 ACKNOWLEDGMENTS

This work was supported in part by CONICET (Argentina) under project number PIP 112-200801-01332; Universidad Nacional de San Luis (Argentina) under project 322000; Universidad Tecnológica Nacional, Facultad Regional San Rafael (Argentina) under projects PQPRSR 858 and PQCOSR 526 and the National Agency of Scientific and Technological Promotion (Argentina) under project 33328 PICT 2005.

## Figure Captions

Fig. 1: Schematic representation of the evolution of complexity in the theoretical adsorption models.

Fig. 2: Schematic representation of heterogeneous bivariate square surfaces with chessboard topography. The black (white) symbols correspond to strong (weak) adsorption sites. (a) One-dimensional lattice and (b) square lattice. The patch size in this figure is  $l = 2$ .

Fig. 3: Adsorption isotherms for dimers on one-dimensional lattices with  $\beta w = -1$  and different topographies 1D as indicated. The energy difference between different patches has been chosen to be high ( $c_1 = 1000$  and  $c_2 = 1$ ) in order to emphasize the effects of the surface heterogeneity. Solid lines and symbols represent theoretical and simulation results, respectively. For each set of values of the parameters, the limit cases corresponding to  $1_C$  (open symbols) and  $bp$  (solid symbols) topographies are shown.

Fig. 4: Adsorption isotherms for dimers on one-dimensional lattices with  $c_1 = 1000$ ,  $c_2 = 1$  and two different values of the lateral interactions  $\beta w = -1$  (attractive case) and  $\beta w = 1$  (repulsive case). Solid lines and symbols represent theoretical and simulation results, respectively. For each set of values of the parameters, the limit cases corresponding to  $1_C$  (open symbols) and  $bp$  (solid symbols) topographies are shown.

Fig. 5: Adsorption isotherms for dimers on one-dimensional lattices with  $\beta w = -1$ . The degree of the surface heterogeneity is varied by changing the value of  $c_2$  between 1 and 100 with  $c_1$  fixed ( $c_1 = 1000$ ). Lines represent theoretical results and symbols correspond to simulation data ( $c_2 = 1$ : circles;  $c_2 = 10$ : triangles; and  $c_2 = 100$ : squares). For each set of values of the parameters, the limit cases corresponding to  $1_C$  (open symbols) and  $bp$  (solid symbols) topographies are shown.

Fig. 6: Adsorption isotherms for dimers on one-dimensional lattices with  $\beta w = -1$ ,  $c_1 = 1000$ ,  $c_2 = 1$  and two different values of  $k$  ( $k = 2$  and  $k = 10$ ). Solid lines and symbols represent theoretical and simulation results, respectively. For each set of values of the parameters, the limit cases corresponding to  $1_C$  (open symbols) and  $bp$  (solid symbols) topographies are shown.

Fig. 7: Results of the BET plots for the adsorption in 1D heterogeneous surfaces with  $c_1 = 1000$ ,  $c_2 = 1$ . Dependence on  $k$  of the fraction  $v_m^*/v_m$  for three different values of  $\beta w$ :  $\beta w = 0$ , circles;  $\beta w = -0.5$ , squares and  $\beta w = -1.0$ , triangles. For each set of values of the parameters, the limit cases corresponding to  $1_C$  (open symbols) and  $bp$  (solid symbols) topographies are shown.

Fig. 8: As Fig. 7 for 2D surfaces:  $\beta w = 0$ , circles;  $\beta w = -0.1$ , squares and  $\beta w = -0.5$ , triangles. Symbols connected by (solid) dotted lines correspond to results obtained from (theoretical) MC simulation isotherms.

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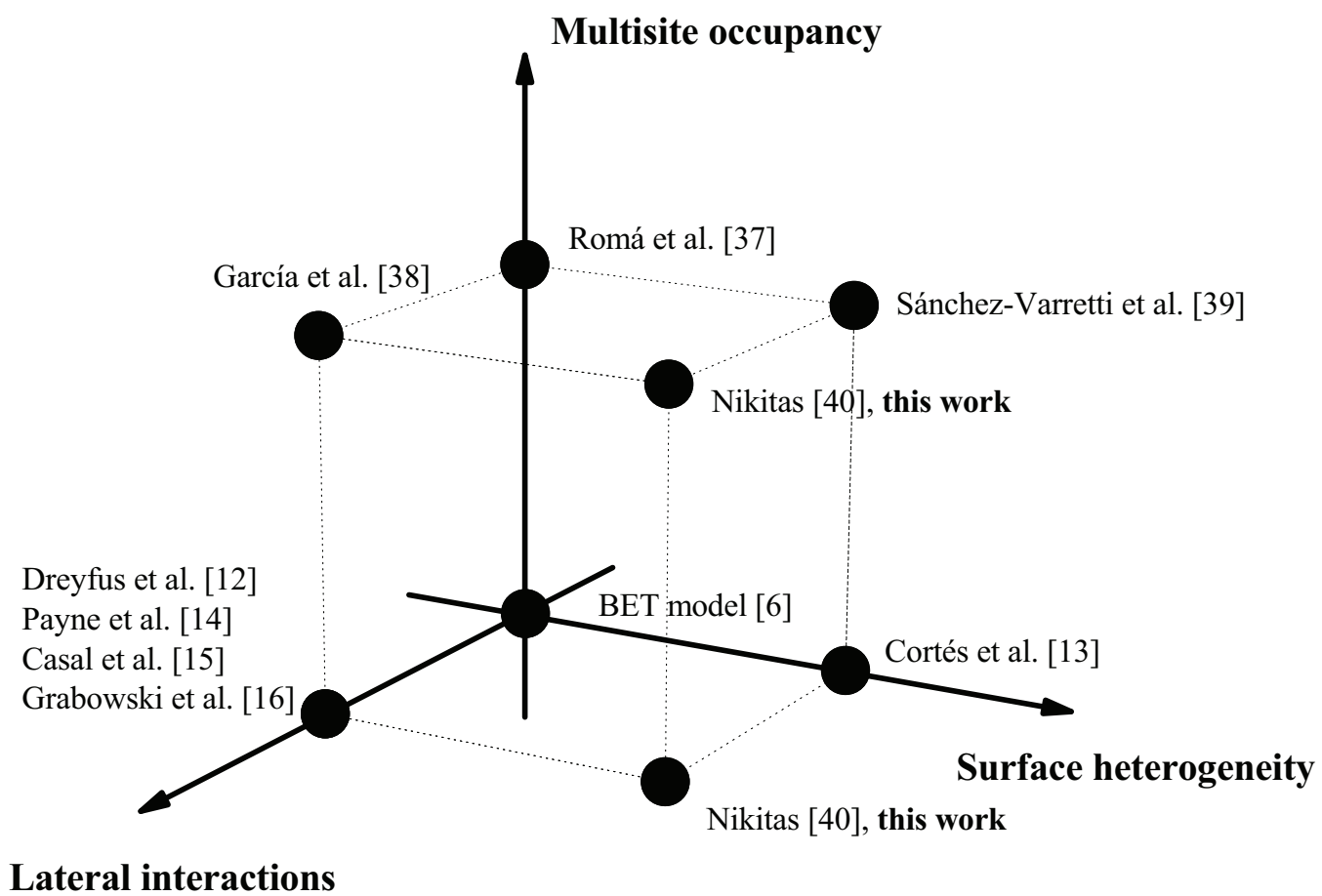


Fig. 1: Sánchez-Varretti et al.

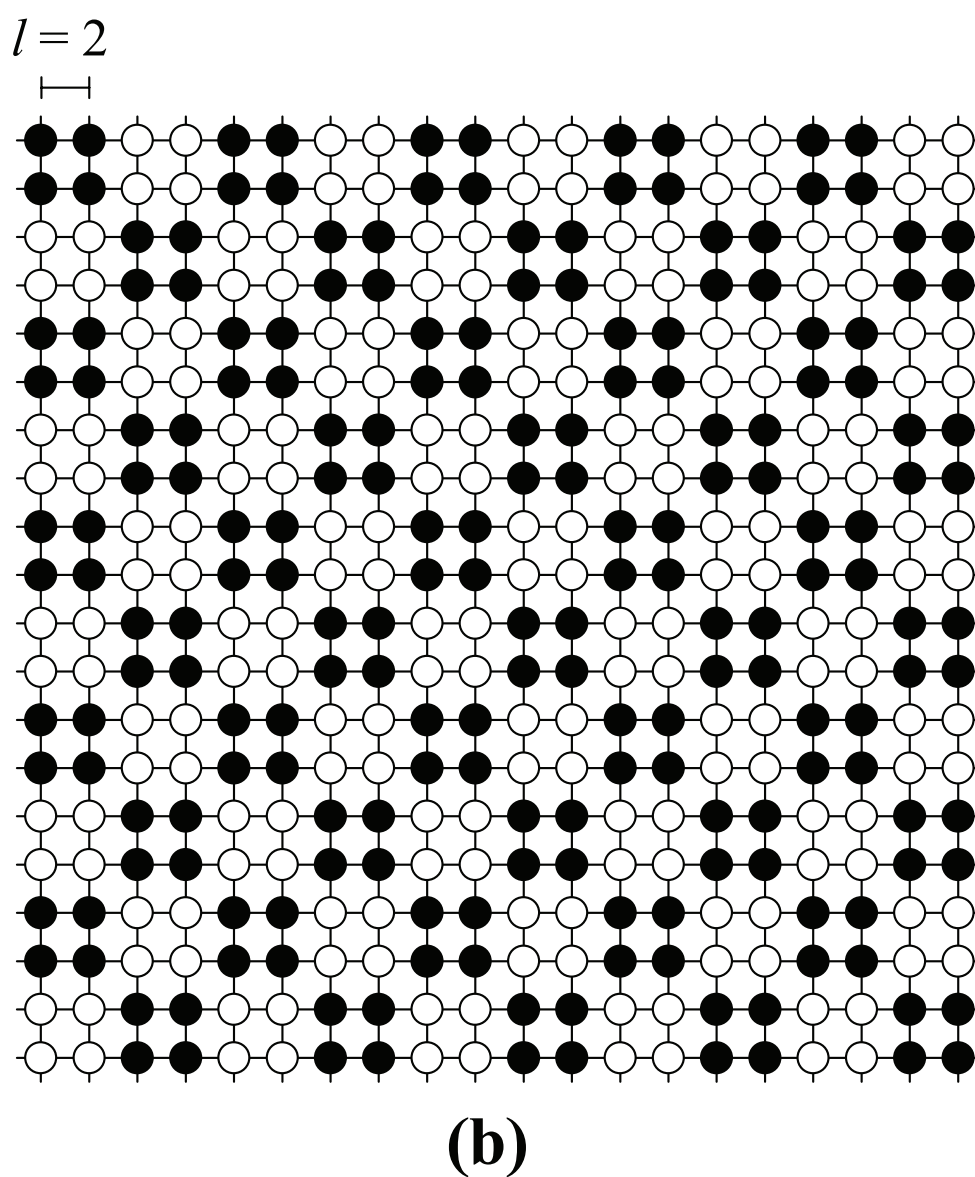
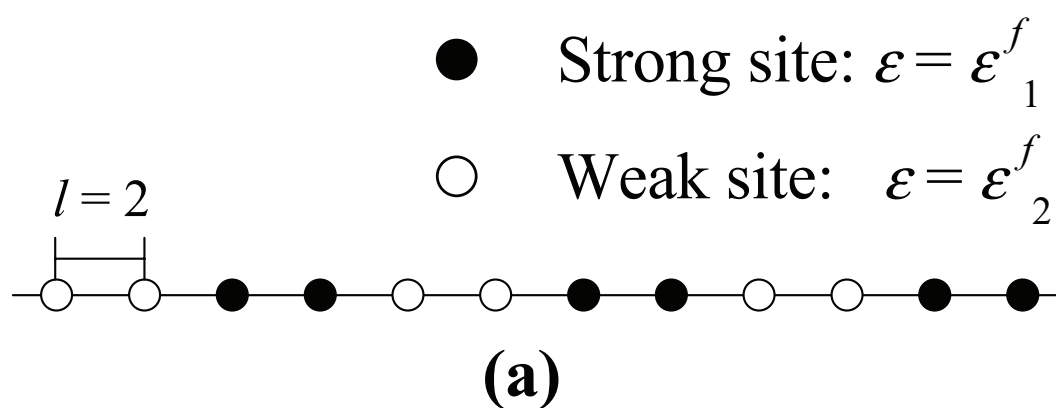


Fig. 2: Sánchez-Varretti et al.

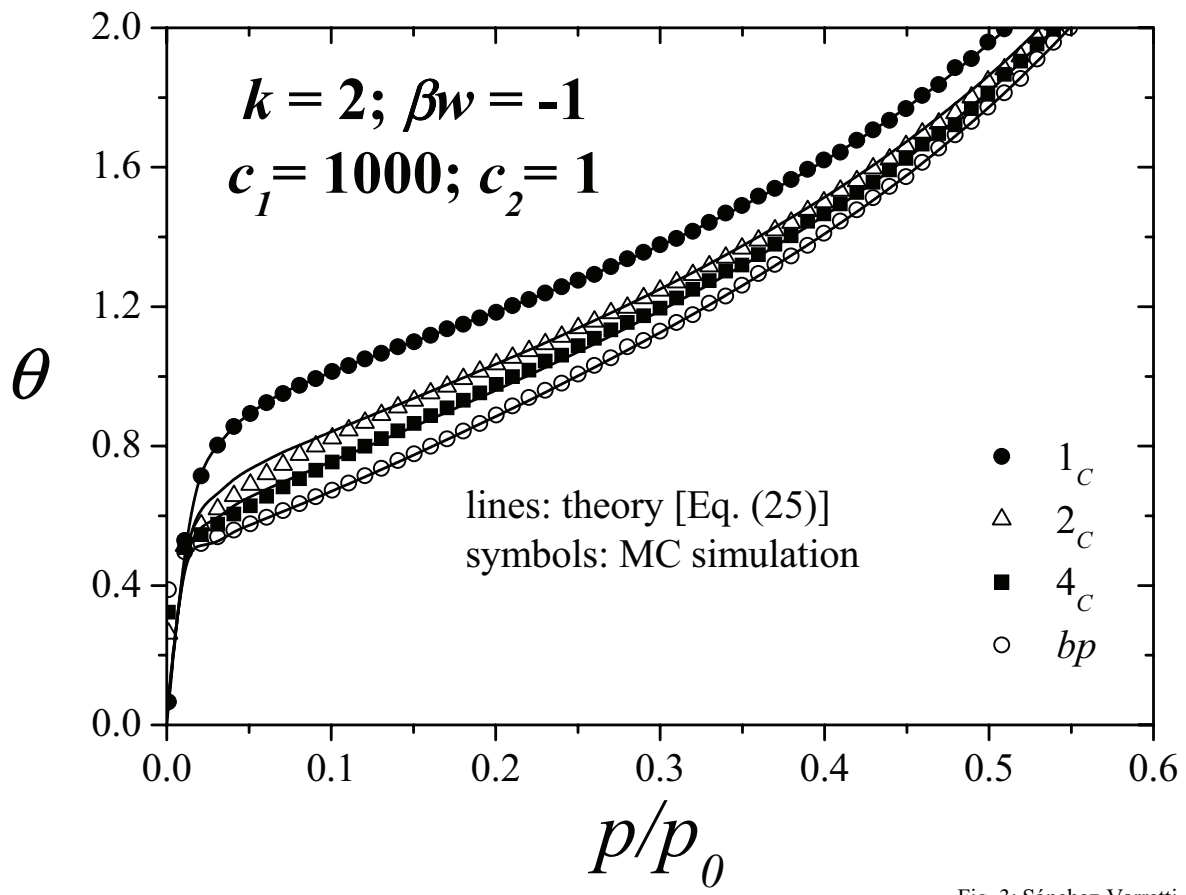


Fig. 3: Sánchez-Varretti et al.

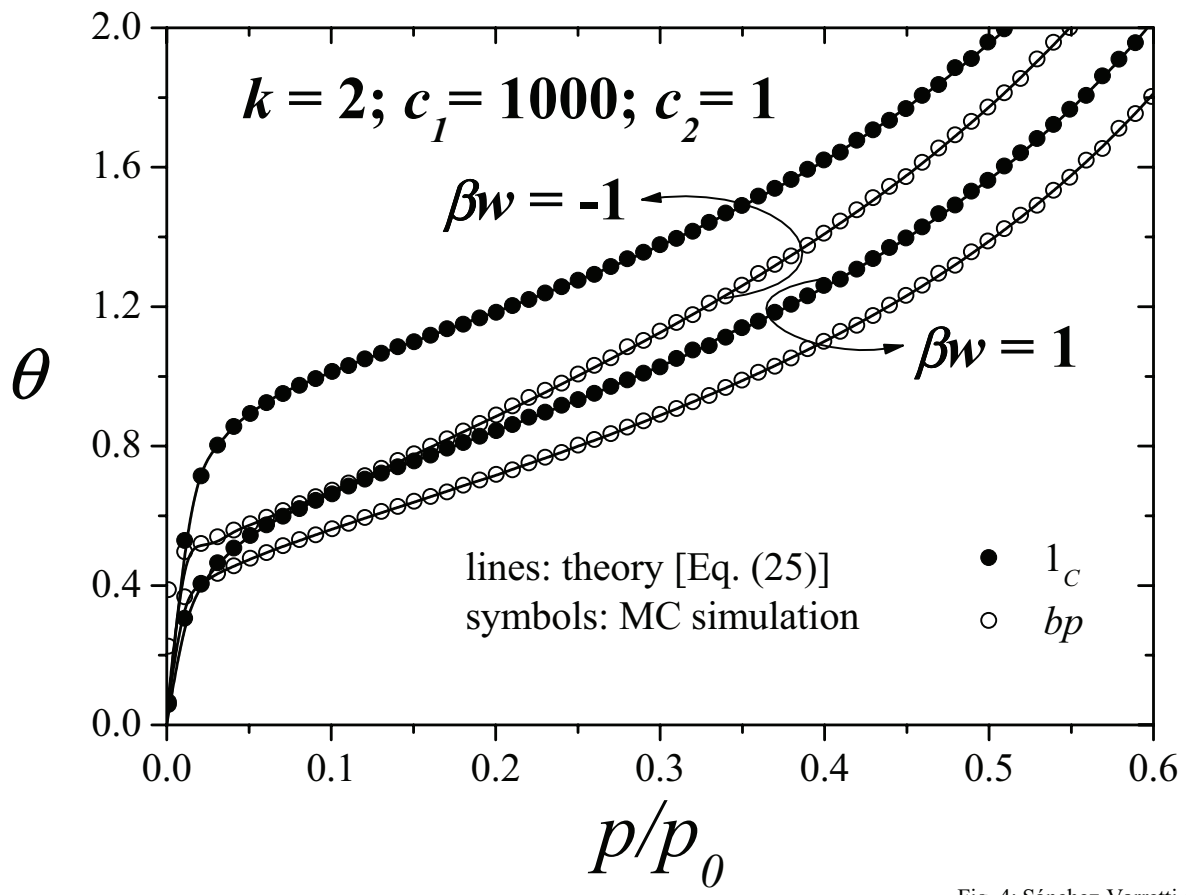


Fig. 4: Sánchez-Varretti et al.

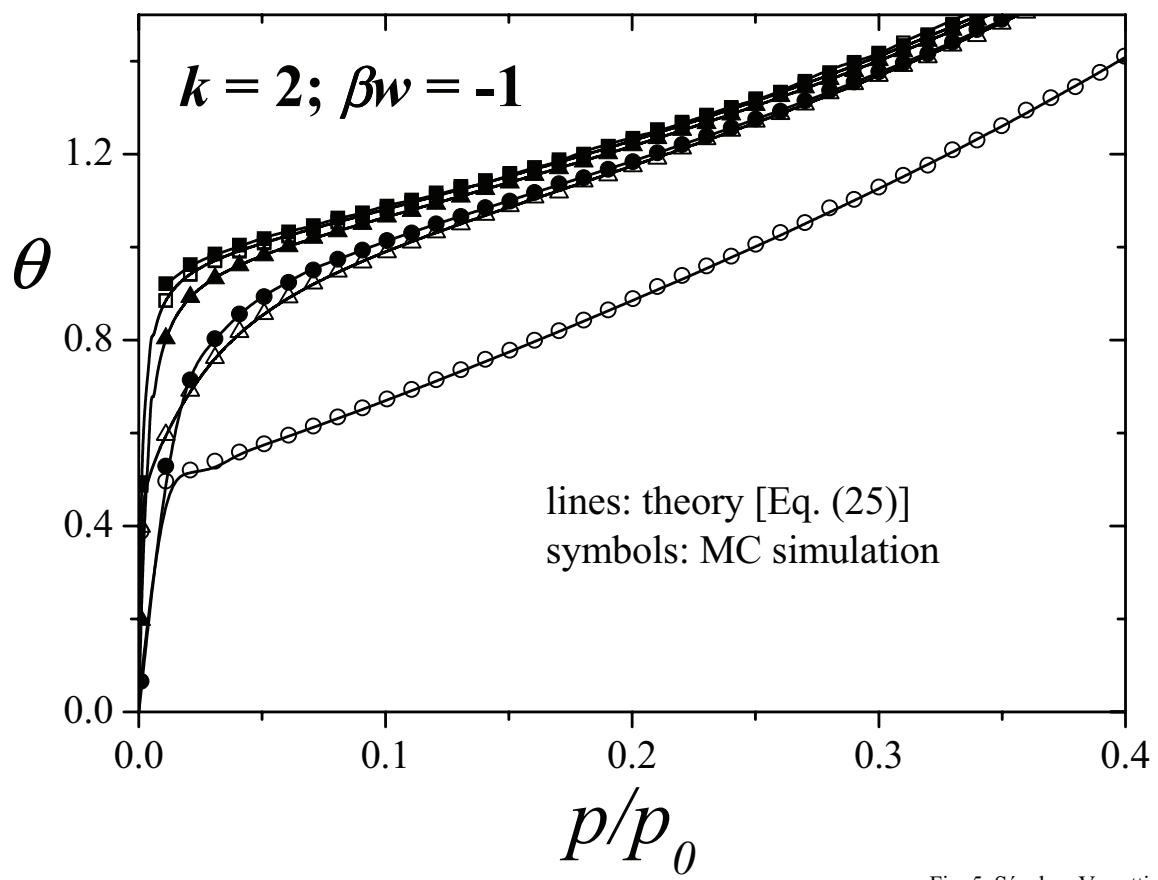


Fig. 5: Sánchez-Varretti et al.

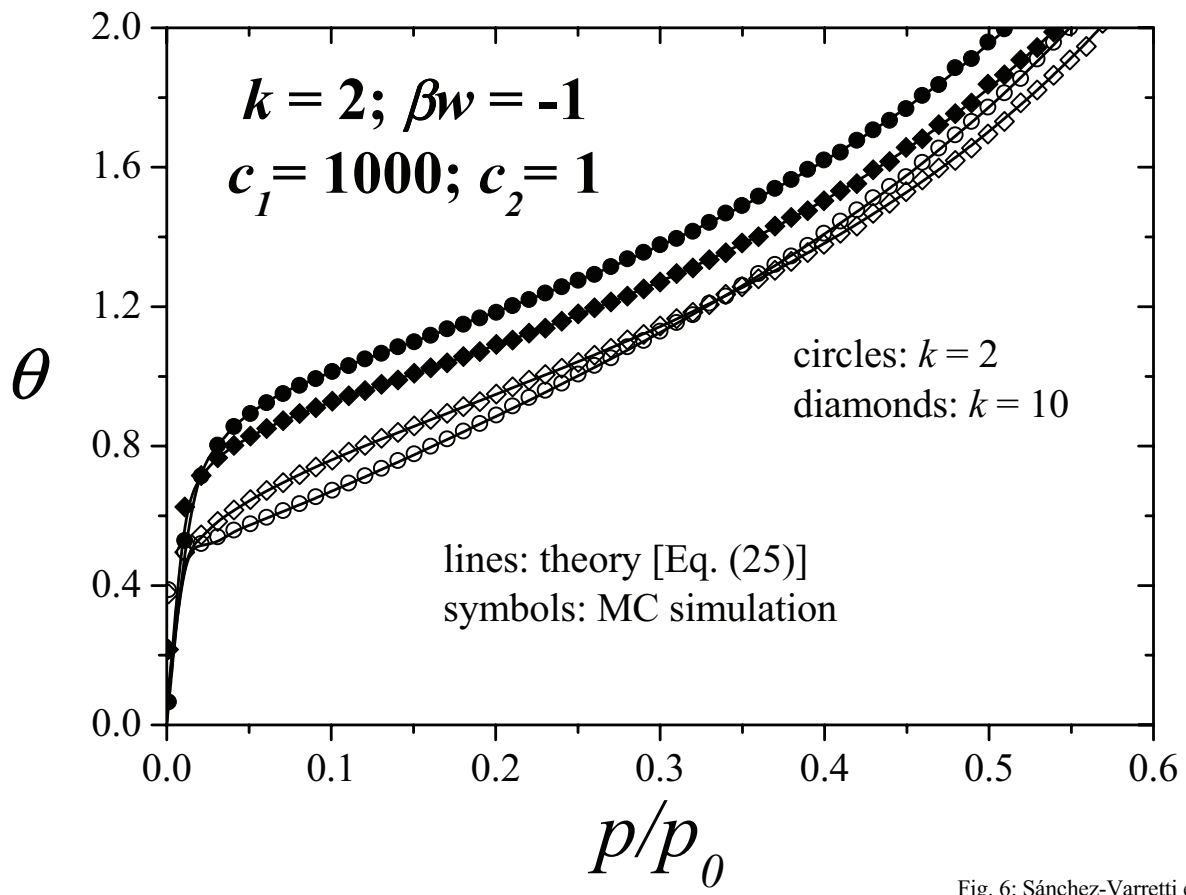


Fig. 6: Sánchez-Varretti et al.

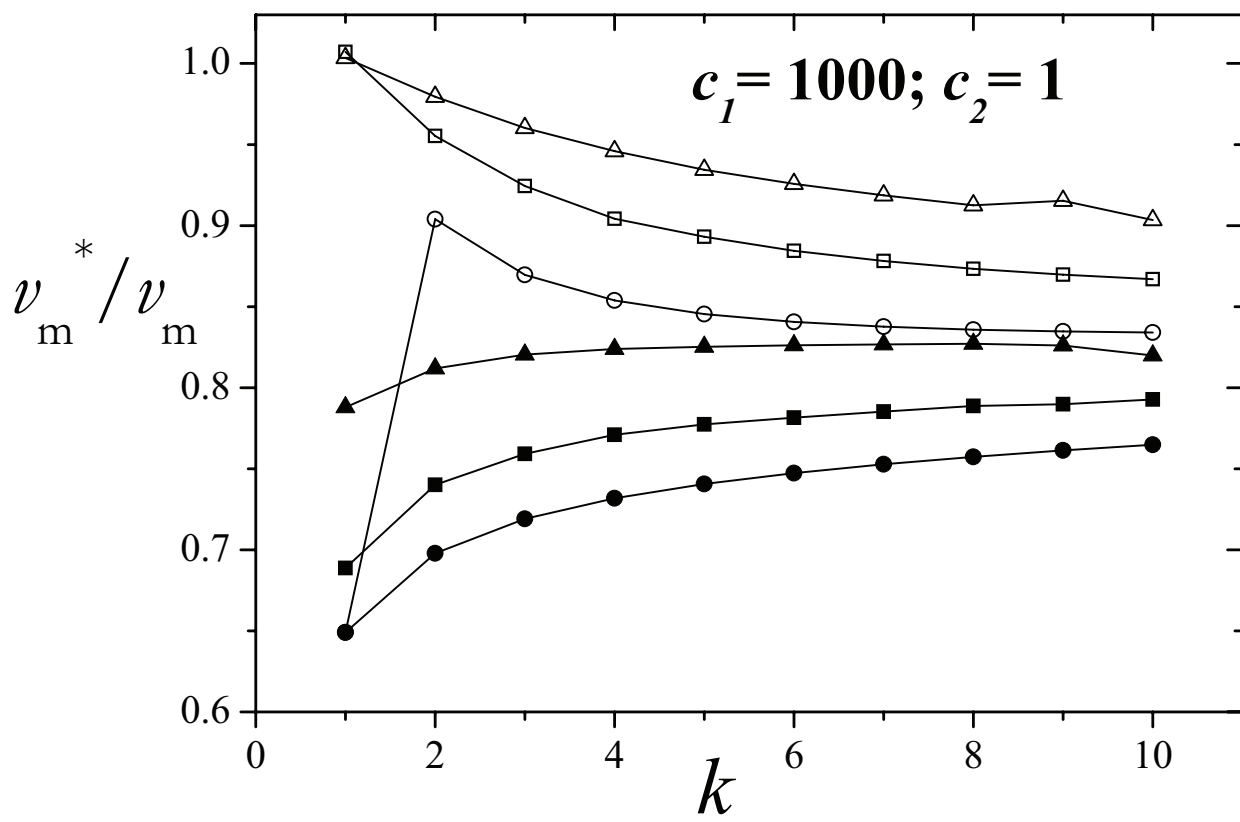


Fig. 7: Sánchez-Varretti et al.

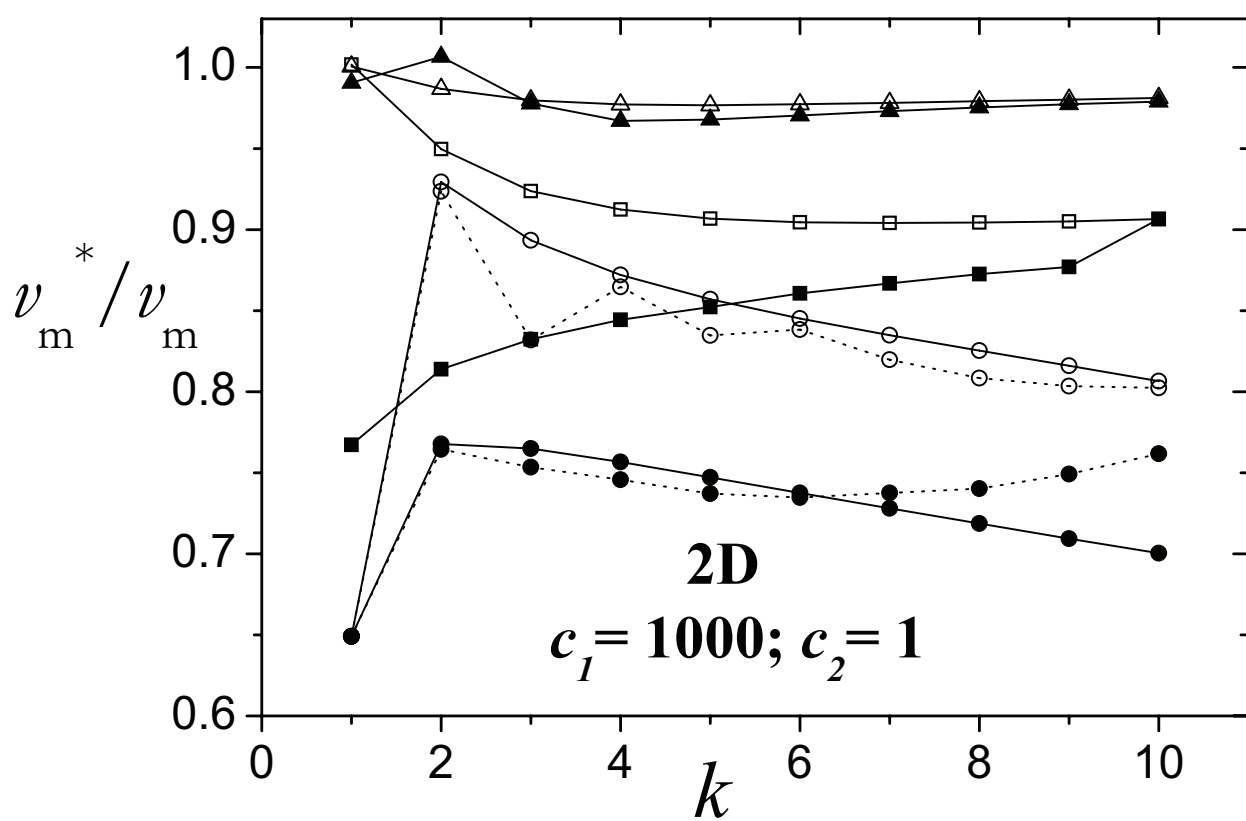


Fig. 8: Sánchez-Varretti et al.